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*Published in:*  
Journal of Chemical Physics

*DOI:*  
[10.1063/1.477731](https://doi.org/10.1063/1.477731)

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*Document Version*  
Publisher's PDF, also known as Version of record

*Publication date:*  
1998

[Link to publication in University of Groningen/UMCG research database](#)

*Citation for published version (APA):*

Champagne, B., Perpète, E. A., van Gisbergen, S. J. A., Baerends, E. J., Snijders, J. G., Soubra-Ghaoui, C., Robins, K. A., & Kirtman, B. (1998). Assessment of conventional density functional schemes for computing the polarizabilities and hyperpolarizabilities of conjugated oligomers: An ab initio investigation of polyacetylene chains. *Journal of Chemical Physics*, 109(23), 10489 - 10498.  
<https://doi.org/10.1063/1.477731>

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Citation: *J. Chem. Phys.* **109**, 10489 (1998); doi: 10.1063/1.477731

View online: <https://doi.org/10.1063/1.477731>

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# Assessment of conventional density functional schemes for computing the polarizabilities and hyperpolarizabilities of conjugated oligomers: An *ab initio* investigation of polyacetylene chains

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(Received 16 June 1998; accepted 11 September 1998)

DFT schemes based on conventional and less conventional exchange-correlation (XC) functionals have been employed to determine the polarizability and second hyperpolarizability of  $\pi$ -conjugated polyacetylene chains. These functionals fail in one or more of several ways: (i) the correlation correction to  $\alpha$  is either much too small or in the wrong direction, leading to an overestimate; (ii)  $\gamma$  is significantly overestimated; (iii) the chain length dependence is excessively large, particularly for  $\gamma$  and for the more alternant system; and (iv) the bond length alternation effects on  $\gamma$  are either underestimated or qualitatively incorrect. The poor results with the asymptotically correct van Leeuwen–Baerends XC potential show that the overestimations are not related to the asymptotic behavior of the potential. These failures are described in terms of the separate effects of the exchange and the correlation parts of the XC functionals. They are related to the short-sightedness of the XC potentials which are relatively insensitive to the polarization charge induced by the external electric field at the chain ends. © 1998 American Institute of Physics. [S0021-9606(98)30447-X]

## I. INTRODUCTION

The determination of the properties of conjugated organic molecules, oligomers and polymers requires including electron correlation effects to reach quantitative accuracy. The origin of these effects is associated with the electron density distribution which has maxima and minima corresponding to the multiple and single bonds, respectively. A large variety of quantum chemical techniques is available for addressing the effects of electron correlation. On the one hand, Møller–Plesset perturbation schemes, configuration interaction approaches, coupled cluster and multiconfigurational self-consistent field techniques have been developed for determining higher and higher levels of electron correlation correction. However, the computational needs are substantial and scale as  $N^a$  with  $N$  being the number of basis functions and  $a \geq 5$ . These approaches become rapidly out of reach when studying systems of interest in materials science. On the other hand, electron correlation corrections can also be assessed by adopting the methods of density functional theory (DFT). In DFT, the electron density is the central quantity which solely determines all the system properties.<sup>1,2</sup>

It is evaluated self-consistently by solving the Kohn–Sham equation which involves kinetic, coulombic, exchange and correlation terms. The quality of the results depends on the choice of the exchange-correlation functional. Several studies have demonstrated that parametrized DFT methods are particularly well suited for optimizing the ground state geometry and evaluating the atomization energies,<sup>3</sup> as well as for calculating vibrational frequencies<sup>4</sup> and determining energies of reaction.<sup>5</sup> In many instances, the DFT values are of similar quality to MP2 results but at an RHF-like computational cost. In particular, Choi *et al.*<sup>6</sup> have recently demonstrated the advantages of DFT schemes with gradient corrections for evaluating the ground state geometry of polyacetylene chains. DFT methods yield a substantial decrease in the bond length alternation (BLA) as compared to Hartree–Fock values and agree very well with MP2<sup>7</sup> as well as with experimental data. On the other hand, the advantages of using DFT for determining single-bond torsional potentials in  $\pi$ -conjugated systems are less obvious.<sup>8</sup>

It has also been proposed that DFT methods can provide accurate polarizabilities and hyperpolarizabilities not only

for atoms and small molecules, but also for large systems.<sup>9–34</sup> The recent investigation of buckminsterfullerene by three of us<sup>32</sup> is an example of the range of applicability of DFT methods for tackling materials science questions. Several studies demonstrate the suitability of DFT for computing the linear polarizability,  $\alpha$ , of small and medium-size molecules. Whereas coupled Hartree–Fock procedures generally underestimate  $\alpha$  by 10%–15%, both local and nonlocal DFT treatments provide values within 5% of the experimental data,<sup>15–19,21–22,26,27,31</sup> with improvements due to gradient corrections being small. The tendency of the local density approximation (LDA) and generalized gradient approximation (GGA) to overestimate polarizabilities of *atoms* and *small* molecules has been related<sup>21,27</sup> to the incorrect asymptotic decay of the exchange–correlation (XC) potential. These systematic overestimates, which are expected to be more important for the hyperpolarizability than for  $\alpha$ , can be removed by using an asymptotically correct (behaving as  $-1/r$ ) XC potential.<sup>27,30</sup>

The appropriateness of conventional local and nonlocal density functionals for computing first and second hyperpolarizabilities,  $\beta$  and  $\gamma$ , is an open question. Comparison with experiment is difficult because, with few exceptions, the calculated  $\beta$  and  $\gamma$  values are static whereas the experiments have been carried out at optical frequencies. It is not unusual for DFT schemes to overestimate the experimental values whereas the coupled Hartree–Fock (CHF) procedure exhibits the opposite deficiency. Indeed, there is more than one example where the static LDA and GGA values even overshoot the frequency-dependent experimental quantities, not to mention the results of high-level [MPn, CCSD(T)] static *ab initio* calculations.<sup>17–19</sup>

Since polyacetylene (PA) chains are a prototypical  $\pi$ -conjugated system for nonlinear optical (NLO) applications many investigations of their linear and nonlinear polarizabilities have been carried out. We note that, at the CHF/6-31G level, the static electronic hyperpolarizability per  $C_2H_2$  unit has been estimated as  $6.91 \pm 0.39 \times 10^6$  a.u. for the dominant longitudinal component,  $\gamma_L^e(0;0,0,0)$  (denoted hereafter by  $\gamma_L^e$ ) and that the frequency dispersion of this component has been evaluated<sup>37–39</sup> for most common NLO processes. Many-body perturbation calculations show that electron correlation has a large effect on  $\gamma_L^e$ . At the MP2/6-31G level the value is increased by a factor of 2.84 with only a small further change of about 8% at the MP4 level.<sup>40</sup> The total correlation effect arises directly from the change in electronic structure as well as indirectly through the shift in equilibrium geometry. At the RHF/6-31G geometry, the MP2/CHF  $\gamma_L^e$  ratio is 1.92 (as compared to 2.84 for the MP2/6-31G geometry). Refining the calculations by using more extended basis sets does not appear to significantly change these estimates of the electron correlation-induced increase of  $\gamma_L^e$ . On the other hand, electron correlation decreases the static electronic longitudinal polarizability,  $\alpha_L^e(0;0)$  (denoted hereafter by  $\alpha_L^e$ ), by about 20%.

Recent studies have addressed the suitability of using DFT methods for computing  $\alpha_L^e$  in model hydrogen chains by comparing with MPn and CC schemes.<sup>41–43</sup> All many-body perturbation calculations show that electron correlation

corrections decrease the asymptotic longitudinal polarizability per unit cell of the infinite «polymeric» chain. Using the (6)-311G(\*) basis set, at the MP4 level, the decrease ranges between 2.8% and 10.5% as a function of the degree of BLA whereas, at the CCSD(T) level, it ranges between 8.1% and 12.3%.<sup>41,42</sup> On the other hand, the use of the BLYP and B3LYP functionals in DFT leads to a substantial increase of the asymptotic longitudinal polarizability per unit cell. This increase, which attains 85% (B3LYP) and 153% (BLYP) for the less alternant chains, seems to be related to the exchange functional since the LYP correlation functional provides only small corrections to the results obtained using the Becke functional without correlation.<sup>43</sup>

The purpose of this paper consists in extending these initial studies by considering the  $\alpha_L^e$  and  $\gamma_L^e$  of polyacetylene chains and, thereby, addressing the usefulness of various LDA and GGA schemes for computing the polarizability and second hyperpolarizability of  $\pi$ -conjugated organic systems. The suitability of both the exchange and correlation functionals is considered as well as the importance of their gradient corrections. In Sec. II we describe the various approaches we have adopted for evaluating  $\alpha_L^e$  and  $\gamma_L^e$ ; and in Sec. III we present our results and discuss several aspects before concluding in Sec. IV.

## II. METHODOLOGY

When a static homogeneous external electric field,  $F$ , is applied along the longitudinal axis of a centrosymmetric molecule, it induces a dipole moment having the longitudinal component:

$$\Delta\mu_L(F) = \alpha_L F + \frac{1}{6} \gamma_L F^3 + \dots, \quad (1)$$

where  $\alpha_L, \gamma_L$  include both electronic and vibrational contributions. Due to centrosymmetry, the static first hyperpolarizability,  $\beta_L$ , vanishes. In conjugated systems such as PA chains, the longitudinal components are by far the largest as a result of electron delocalization along the backbone. The present work focuses upon  $\alpha_L^e$  and  $\gamma_L^e$ , denoted from here on by  $\alpha$  and  $\gamma$ , although recent investigations have highlighted the fact that vibrational contributions can be very substantial in  $\pi$ - and  $\sigma$ -conjugated systems.<sup>44</sup>

In most cases,  $\alpha$  is determined from coupled-perturbed iterative procedures which compute the first-order response of the density matrix,  $D^{(1)}$ , to the external electric field. Thus,  $\alpha$  is given by

$$\alpha = 2 \sum_{p,q} M_{pq} D_{pq}^{(1)}, \quad (2)$$

where  $M_{pq}$  is an element of the longitudinal dipole moment matrix. This expression holds for closed-shell systems in which the sum runs over all the atomic orbital indices. At the Hartree–Fock level, the evaluation of  $D^{(1)}$  is performed through the coupled-perturbed Hartree–Fock (CPHF) procedure,<sup>45</sup> whereas the coupled-perturbed Kohn–Sham (CPKS) technique<sup>46</sup> is adopted when using DFT functionals.

In principle, the evaluation of  $\gamma$  can also be performed within a coupled-perturbed scheme where, in addition to  $D^{(1)}$ , the second field-derivatives of the density matrix, i.e.,

$D^{(2)}$ , are computed iteratively. This has been done at the Hartree–Fock level using the CPHF procedure implemented in the GAMESS program.<sup>47</sup> Since DFT programs for computing  $\gamma$  analytically from the CPKS equations are not yet available, the latter was calculated by a finite field (FF) procedure where  $\alpha$  or  $\beta$  is evaluated at different field amplitudes giving the estimates:

$$\gamma^{0,k} = 2 \frac{[\alpha(2^k F) - \alpha(0)]}{(2^k F)^2}, \quad (3)$$

$$\gamma^{0,k} = \frac{\beta(2^k F)}{2^k F}, \quad (4)$$

with  $k \geq 0$ . Accurate first and second derivatives require that the field amplitude be small enough to avoid contaminations from the higher-order hyperpolarizabilities. However, the smaller the field amplitude, the lower the accuracy of  $\gamma$  because the number of significant digits in the field-dependent first hyperpolarizability or in the polarizability difference decreases. A good compromise was found by taking  $F = 8 \times 10^{-4}$  a.u. and  $k = 0-3$  while simultaneously employing a Romberg type procedure<sup>48</sup> to remove the higher-order contaminations. Thus, successive improvements of the  $\gamma$  estimates from the initial  $\gamma^{0,k}$  values were calculated using the general iterative expression:

$$\gamma^{p,k} = \frac{4^p \gamma^{p-1,k} - \gamma^{p-1,k+1}}{4^p - 1}, \quad (5)$$

where  $p$  is the order of the Romberg iteration. This procedure results in an accuracy of 0.1% in  $\gamma$ . It is important to note that when the FF approach is applied at the HF or post-HF levels much better numerical accuracy is achieved.<sup>49</sup> That is because all the terms are obtained analytically whereas the evaluation of the energy and the wave function in DFT calculations occurs via spatial integrations performed numerically using grids of points. Since the DFT methods obey the Hellmann–Feynman theorem:

$$\gamma = - \left( \frac{\partial^4 E}{\partial F^4} \right)_{F=0} = \left( \frac{\partial^3 \mu}{\partial F^3} \right)_{F=0} = \left( \frac{\partial^2 \alpha}{\partial F^2} \right)_{F=0} = \left( \frac{\partial \beta}{\partial F} \right)_{F=0}, \quad (6)$$

the finite field numerical approach is equivalent to the analytical CPKS procedure, provided the numerical accuracy is sufficient. The MP2 evaluation of  $\alpha$  is performed analytically in GAUSSIAN94<sup>50</sup> using a correlated equivalent of the CPHF procedure whereas for  $\gamma$  Eqs. (3) and (5) are utilized.

Various DFT schemes based on different exchange–correlation functionals have been employed. The first exchange–correlation functional, denoted SVWN, is composed of the local Slater exchange functional<sup>51</sup> plus the uniform electron gas local correlation functional due to Vosko, Wilk, and Nusair.<sup>52</sup> It can be improved by including gradient corrections for exchange, by means of Becke's<sup>53</sup> expression, and for correlation by adopting the Lee, Yang, and Parr<sup>54</sup> or the Perdew and Wang<sup>55</sup> functionals. Thus, SLYP, SPW91, and BVWN include nonlocal corrections for either the correlation or exchange functionals whereas BLYP and BPW91 incorporate nonlocal corrections in both terms.

In the three parameter B3LYP functional,<sup>56</sup> the exchange potential includes some percentage of the exact Hartree–Fock exchange; the remaining part being described by the Slater functional plus a weighted Becke gradient correction. In GAUSSIAN94<sup>50</sup> the standard percentage of Hartree–Fock exchange is 20% (80% of DFT exchange) but we have also considered 50% (50% of DFT exchange) and 80% (20% of DFT exchange) in order to distinguish between the effects of the HF and DFT exchange functionals. The correlation part of the B3LYP functional includes a weighted combination of the local VWN and nonlocal LYP correlation potentials.

We have addressed the significance of the correlation correction within the DFT scheme by combining HF exchange with either the VWN or the LYP functional giving rise to the HFVWN and HFLYP methods. In these HFVWN and HFLYP approaches, as well as in the standard and modified B3LYP schemes, the wave function is obtained fully self-consistently within the corresponding Coulomb and Pauli fields described by the various functionals, i.e., exactly in the same way as for the DFT schemes mentioned in the previous paragraph. This has to be contrasted with the hybrid approach described in the next paragraph where the HF orbitals are substituted into the density functionals. It is important, however, to stress that this splitting of the exchange–correlation functional into exchange and correlation parts is ill-founded. It has been recently demonstrated<sup>57,58</sup> in a set of diatomic molecules that GGA exchange density functionals also incorporate near-degeneracy (nondynamical) correlation. At the same time, GGA correlation density functionals contain dynamical correlation but omit the nondynamical part. An alternative interpretation of exchange and correlation in the DFT context, based on the separation into parallel and anti-parallel spin terms has been given by Gill *et al.*<sup>59</sup> who have compared Møller–Plesset electron correlation corrections and electron correlation energies associated with several DFT correlation functionals. For all the DFT methods described above, the GAUSSIAN94 series of programs<sup>50</sup> has been adopted to compute  $\alpha$  from the CPKS procedure and  $\gamma$  from the numerical FF scheme based on Eqs. (3) and (5).

Less than ten years ago, a hybrid HF–DFT method was presented, which utilizes electron densities derived from standard HF theory in the DFT energy functionals.<sup>59–62</sup> In combination with the BLYP (or B3LYP) exchange–correlation functional this hybrid method has given good agreement with coupled-cluster results and with experiment for atomization energies, ionization potentials, electron affinities, proton affinities, bond lengths, harmonic frequencies, and dipole moments, as well as energies of reaction and activation. It has also been found recently<sup>63</sup> to yield reasonable polarizability and hyperpolarizability values for a number of small molecules. Thus, we have also applied this hybrid HF–DFT procedure using both the BLYP and B3LYP functionals. Since the energy of the system is obtained directly without iteration, i.e., the hybrid method does not optimize the wave function, the Hellmann–Feynman theorem is not satisfied and, therefore, the relations in Eq. (6) do not hold. For this case our  $\alpha$  and  $\gamma$  values were obtained by means of a numerical FF procedure applied to the field-

dependent hybrid energies. In other words,  $\alpha$  and  $\gamma$  were calculated as the negative of the second- and fourth-order derivatives of the energy w.r.t. the external electric field. In order to improve the accuracy, a very large integration grid was chosen. Within the Lebedev integration scheme 999 radial points and 974 angular points were considered for each atom. For comparison, the default adopted for computing  $\alpha$  in conventional DFT schemes contains 75 radial points and 302 angular points.

Other DFT calculations were carried out with the Amsterdam density functional (ADF) program<sup>64</sup> which uses Slater-type orbitals and a density fitting procedure for the Coulomb-type integrals based on auxiliary basis functions. In the ADF code,  $\alpha$  is obtained by solving the linear response equations of time-dependent density functional theory (TDDFT)<sup>65</sup> in the static limit, which is equivalent to solving the CPKS equations. This procedure also provides the field-dependent  $\beta$ , which was numerically differentiated according to Eq. (5) to obtain  $\gamma$ .

The ADF calculations were performed with three different sets of exchange-correlation functionals and kernels. The exchange-correlation kernels, which are the first or higher functional derivatives of the exchange-correlation potential w.r.t. the density, enter into the evaluation of  $\alpha$  and  $\beta$ . The first scheme consists of using the local density approximation (LDA) for both the potential and kernels and can be represented by LDA/LDA, which is identical to the SVWN approach mentioned above, except for differences in basis sets or numerical precision. These functionals can be improved by using the asymptotically correct van Leeuwen-Baerends (LB94) XC potential<sup>66</sup> in the LB94/LDA procedure and further by using the LB94 expressions for both the potential and kernels (LB94/LB94), which leads to results which are equivalent to those from a finite field LB94 calculation. The mixed LB94/LDA scheme, which cannot be obtained from an FF approach, has been highlighted as a better method for computing linear and nonlinear optical properties of small molecules.<sup>27,33</sup> When using the ADF code,  $\alpha$  and  $\beta$  are obtained analytically by solving the CPKS equations whereas calculating  $\gamma$  requires numerical differentiation of field-dependent  $\beta$  values according to Eq. (4).

The  $\alpha$  and  $\gamma$  calculations carried out with the GAUSSIAN94 program used the split-valence 6-31G basis set<sup>67</sup> whereas those performed with the ADF code employed double-zeta Slater-type orbitals, from the standard ADF basis set II, with the corresponding auxiliary basis set.<sup>68</sup> These basis sets are adequate for computing accurate electronic (hyper)polarizabilities of extended  $\pi$ -conjugated oligomers. Indeed, when the chain is lengthened, the difference between the split valence or double- $\zeta$  type basis sets and more extended bases containing polarized and diffuse functions becomes small as a result of compensation by neighboring atomic functions. This phenomenon was first noted by Hurst *et al.*<sup>35</sup> in CPHF calculations on PA chains and has been further confirmed for DFT calculations performed with the ADF and GAUSSIAN94 codes. Indeed, using the LDA/LDA (SVWN) approach with STO basis sets in the ADF program, the  $\gamma$  ratio for double- $\zeta$  and double- $\zeta$  plus diffuse polarization functions is equal to 0.73, 1.03, and 1.05 for  $C_{10}H_{12}$ ,

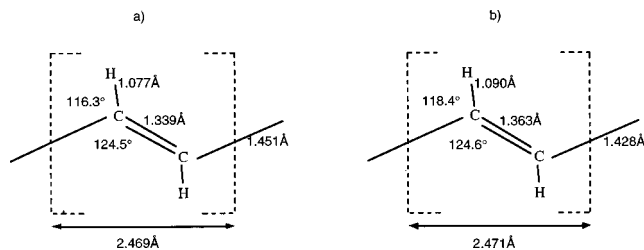


FIG. 1. (a) RHF/6-31G and (b) B3LYP/6-311G\* unit cell parameters of PA.

$C_{20}H_{22}$ , and  $C_{30}H_{32}$ , respectively.<sup>69</sup> Similarly, using Gaussian basis sets, the  $\gamma(6-31G+PD)/\gamma(6-31G)$  ratio (see Ref. 35 for the 6-31G+PD basis) increases from 0.48 to 0.79 for  $C_6H_8$  and  $C_{12}H_{14}$ , respectively.<sup>70</sup> Because of the similarity to the corresponding CHF ratio, which goes from 0.50 for  $C_6H_8$  to 0.80 for  $C_{12}H_{14}$  and 0.89 for  $C_{20}H_{22}$ , one can assume a similar convergence toward a value close to unity.

### III. RESULTS

The geometries of increasingly large PA chains have been completely optimized at the B3LYP/6-311G\* and RHF/6-31G levels of approximation. When the size of the chain increases the geometrical parameters of the central unit cell converge toward the polymeric values. Figure 1 presents the unit cells and the two sets of converged polymeric parameters which correspond to a BLA of 0.112 Å (RHF/6-31G) and 0.065 Å (B3LYP/6-311G\*). MP2/6-31G\* calculations due to Hirata *et al.*<sup>7</sup> provide the BLA values 0.080 Å, 0.076 Å and 0.073 Å for  $C_{10}H_{12}$ ,  $C_{12}H_{14}$  and  $C_{14}H_{16}$ , respectively, showing that there is a substantial and systematic decrease of BLA upon including electron correlation either with DFT or many-body schemes. The polymeric parameters in Fig. 1 have been used to build PA oligomers of various lengths with the CH bond length and CCH bond angle for the end hydrogen atoms being fixed at 1.084 Å and 121°. For the representative  $C_{20}H_{22}$  oligomer we have evaluated  $\alpha$  and  $\gamma$  at 18 different DFT levels of approximation. The values at the two geometries are listed in Tables I and II, respectively, and are compared there to the CHF/6-31G and MP2/6-31G results.

#### A. Polarizability

It is generally accepted that the smaller the BLA, the larger the electron delocalization and the larger the value of  $\alpha$ . At the CHF/6-31G level, going from BLA=0.112 Å to BLA=0.065 Å leads to an increase in  $\alpha$  of 31%. Adding electron correlation corrections within the MP2, MP4 and CCSD(T) schemes decreases the  $\alpha$  of PA chains, as compared to the CHF/6-31G value, with the less alternant systems remaining the most polarizable. According to Ref. 40, in the infinite chain limit the MP2 electron correlation correction reduces  $\alpha$  for the MP2/6-31G and RHF/6-31G optimized structures by 14% and 23%, respectively. These “infinite chain” results are supported by CCSD(T)/6-31G finite field calculations on the smallest PA oligomers which also show reductions of  $\alpha$  from the CHF value. At the RHF/6-31G optimized geometry, the CCSD(T)/CHF ratio in the 6-31G basis is 0.837, 0.802, and 0.776 for all-trans butadiene,

TABLE I. Values for the electronic static longitudinal polarizability,  $\alpha$ , of  $C_{20}H_{22}$  obtained by the CHF/6-31G, MP2/6-31G, and various DFT methods. The DFT calculations marked by an asterisk were obtained using a 6-31G basis in the GAUSSIAN94 program; the remaining DFT calculations employed double zeta basis II in the ADF code. All values are in atomic units (1.0 a.u. of polarizability =  $1.6488 \times 10^{-41} \text{ C}^2 \text{ m}^2 \text{ J}^{-1} = 0.148 \text{ 18 } \text{\AA}^3$ ).

	B3LYP/6-311G* geometry BLA=0.065 Å	RHF/6-31G geometry BLA=0.112 Å
MP2	917	778
CHF	1327	1015
S*	2055	1652
B*	2050	1632
HFVWN*	1320	1007
HFLYP*	1312	1004
SVWN*	2039	1631
SLYP*	2046	1644
SPW91*	2043	1641
BVWN*	2033	1612
BLYP*	2041	1625
BPW91*	2036	1621
B3LYP (20%)*	1789	1379
B3LYP' (50%)*	1511	1151
B3LYP'' (80%)*	1358	1038
Hybrid HF-DFT (BLYP)*	1438	1109
Hybrid HF-DFT (B3LYP)*	1408	1084
LDA/LDA	2068	1644
LB94/LDA	2064	1628
LB94/LB94	1996	1577

hexatriene, and octatetraene whereas, for the B3LYP/6-311G\* optimized structure, the corresponding ratios are 0.829, 0.788, and 0.755.

On the other hand, the SVWN  $\alpha$  values (cf. Table I) are *larger than* the CHF results for both structures. Adding non-local corrections with the Becke and/or LYP/PW91 functionals does not change the LDA values by more than 1%. These conventional DFT schemes predict an increase of  $\alpha$  by about 54% for the BLA of 0.065 Å and about 61% for the BLA of 0.112 Å. This is in complete disagreement with the effect of correlation as obtained from many-body perturbation theory/coupled cluster procedures.

In order to assess the origin of the increase in  $\alpha$  vs. CHF (cf. Table I), we have varied the exchange and correlation functionals independently. Although the interpretation of the exchange and correlation functionals in terms of the traditional meaning of these concepts may not be straightforward, as noted above, we continue to denote them by their common names. Note that the correlation functionals, both at the local-density and the gradient-corrected levels, have very little effect. This follows from the near equality of the HFVWN and HFLYP  $\alpha$  values to the CHF result. The VWN and LYP correlation functionals do not seem to introduce the type of correlation described by MP2 or CCSD(T) calculations and these correlation functionals are as ineffective when combined with S or B exchange as with HF exchange. In contrast, replacing HF exchange by a density functional

TABLE II. Values for the electronic static longitudinal second hyperpolarizability,  $\gamma$ , of  $C_{20}H_{22}$  obtained by the CHF/6-31G, MP2/6-31G, and various DFT methods. The DFT calculations marked by an asterisk were obtained using a 6-31G basis in the GAUSSIAN94 program; the remaining DFT calculations employed double zeta basis II in the ADF code. All values are in  $10^5$  atomic units (1.0 a.u. of second hyperpolarizability =  $6.235 \text{ 377} \times 10^{-65} \text{ C}^4 \text{ m}^4 \text{ J}^{-3} = 7.0423 \times 10^{-54} \text{ m}^5 \text{ V}^{-2} = 5.0367 \times 10^{-40} \text{ esu}$ ).

	B3LYP/6-311G* geometry BLA=0.065 Å	RHF/6-31G geometry BLA=0.112 Å
MP2	336	166
CHF	200	93.4
S*	578	670
B*	585	657
HFVWN*	194	89.6
HFLYP*	198	92.5
SVWN*	584	662
SLYP*	576	660
SPW91*	580	667
BVWN*	591	654
BLYP*	585	653
BPW91*	590	655
B3LYP (20%)*	563	434
B3LYP' (50%)*	392	222
B3LYP'' (80%)*	255	126
Hybrid HF-DFT (BLYP)*	423	200
Hybrid HF-DFT (B3LYP)*	394	207
LDA/LDA	627	695
LB94/LDA	639	707
LB94/LB94	545	688

for the exchange substantially increases the polarizability. This happens for both the local-density (i.e., Slater) exchange approximation and the gradient-corrected one of Becke, irrespective of which correlation functional (VWN, LYP or PW91) is used. The large overestimation of  $\alpha$  by the exchange functionals is reduced upon increasing the amount of Hartree–Fock exchange in the B3LYP functional from 20% to 80%, or to 100% in HFLYP. To a high degree of accuracy the value of  $\alpha$  increases linearly with the square of the percentage of Becke exchange for both geometries. However, no similar relation has been found for  $\gamma$  (see next section). The hybrid HF-DFT also leads to  $\alpha$  values that are larger than at the CHF level of approximation. They are not nearly so much overestimated as with the pure DFT approach since, as one might have anticipated, the hybrid results are much closer to those found with Hartree–Fock exchange than with Slater or Becke exchange. The hybrid-HF-DFT method has a density response identical to the one in HF, so the large overestimations in the pure DFT results seem to be due more to an erroneous (field dependence of the) XC potential than to the XC energy expression itself.

The LDA/LDA calculations performed with the ADF program lead to very similar values to those obtained from GAUSSIAN94 using the SVWN functional. This was expected since the functional is the same in either case although the two approaches are based on different atomic basis sets and

TABLE III. Electronic static longitudinal polarizability,  $\alpha$ , of  $C_{12}H_{14}$ . See caption of Table I for basis set information. All the values are in a.u.

	B3LYP/6-311G* geometry BLA=0.065 Å	RHF/6-31G geometry BLA=0.112 Å
MP2	388	357
CHF	512	448
SVWN	632	569
B3LYP (20%)	588	522
HFVWN	509	445
Hybrid HF-DFT (B3LYP)	512	452
LDA/LDA	680	592

integration procedures. The use of the LB94 exchange-correlation functional (LB94/LDA or LB94/LB94), which has the correct long-range behavior, does not improve the LDA/LDA values. This can be understood from the fact that the polarizability of these  $\pi$ -conjugated systems is mainly determined by charge displacements within the molecule, which makes the asymptotic behavior of the potential of limited importance. It shows at the same time that the overestimations in the polarizabilities have a different origin here than in the case of small molecules.

## B. Second hyperpolarizability

Correlation as introduced by MP2 calculations<sup>40</sup> increases the second hyperpolarizability, by 68% and 88% for BLA=0.065 Å and BLA=0.112 Å, respectively. Again, correlation at either the LDA level (VWN) or with gradient corrections (LYP) has very little effect. Just like in the case of  $\alpha$ , the use of the VWN and/or LYP functional in conjunction with HF exchange leads to a small decrease of  $\gamma$  in comparison with the CHF value. For  $\alpha$  this decrease was seen to be much too small to agree with the MP2 [and CCSD(T)] electron correlation treatments; for  $\gamma$ , the DFT correlation correction is not only too small but also in the wrong direction. When introducing a DFT exchange functional, either at the LDA or GGA level, a strong increase of  $\gamma$  is obtained, irrespective of the correlation functional. Indeed, Table II shows that the SVWN functional leads to an increase for  $C_{20}H_{22}$  with respect to the CHF value by 192% for BLA=0.065 Å and by 608% for BLA=0.112 Å. These increases are much larger than those obtained with MP2. In particular, for the more alternant system they cause  $\gamma$  to become larger than that of the less alternant  $C_{20}H_{22}$  chain.

From the above we conclude that, as in the case of  $\alpha$ , the pathological behavior of  $\gamma$  is linked in large part to the exchange functional. Upon adopting the B3LYP functional and varying the Hartree–Fock exchange contribution from 20% to 80%, the increase of  $\alpha$  w.r.t. the CHF value was seen earlier to be reduced substantially. The same happens here for  $\gamma$ . The relative overestimation of  $\gamma$  for the more alternant system is also reduced, the ratio  $\gamma(\text{BLA}=0.065 \text{ Å})/\gamma(\text{BLA}=0.112 \text{ Å})$  becoming substantially greater than unity. Without any Hartree–Fock exchange (i.e., BLYP) the latter ratio is 0.90 while for HF exchange contributions of 20%, 50%, and 80% in B3LYP, this ratio increases to 1.30, 1.77, and 2.02. For comparison, at the CHF level the same

TABLE IV. Electronic static longitudinal second hyperpolarizability,  $\gamma$ , of  $C_{12}H_{14}$ . See caption of Table I for basis set information. All the values are in  $10^4$  a.u.

	B3LYP/6-311G* geometry BLA=0.065 Å	RHF/6-31G geometry BLA=0.112 Å
MP2	352	249
CHF	182	132
SVWN	328	366
B3LYP (20%)	329	314
HFVWN	177	127
Hybrid HF-DFT (B3LYP)	320	255
LDA/LDA	341	402

ratio is 2.14 whereas, at the MP2 level, it is 1.91. Thus, although the conventional B3LYP (20%) procedure correctly gives a larger  $\gamma$  for the less alternant system, it significantly underestimates the effect of varying the BLA.

For  $\gamma$ , as opposed to  $\alpha$ , the hybrid HF-DFT methods improve on the CHF treatment and they also behave correctly w.r.t. varying the BLA. This, as for  $\alpha$ , seems to imply the qualitative reasonableness of the HF density response, as well as the qualitative reasonableness of the XC energy functional, and accordingly the poor results for the full LDA and GGA  $\gamma$ 's seem to imply a deficiency of the corresponding field-dependence of the Kohn–Sham potentials. On the other hand, introducing the correct long-range behavior of exchange via the LB94 functional once again has only a relatively small effect on the LDA results.

## C. Chain length dependence of the linear polarizability and second hyperpolarizability

Another important aspect concerns the chain length dependence of the electron correlation correction. It has been found several times<sup>40–42</sup> that the correlated  $\alpha$  and  $\gamma$  divided by the CHF value converges much more rapidly with chain length than either the numerator or denominator by itself. In particular the MP2/CHF ratio for PA chains is nearly converged at  $N=4-6$  unit cells. This behavior has been used to extrapolate the correlated result to the infinite chain limit, which circumvents the problem that correlated property calculations on long chains are not computationally possible.

We have performed additional SVWN, B3LYP (20%), HFVWN, hybrid HF-DFT (B3LYP), and LDA/LDA calculations (see Tables III and IV) on the  $C_{12}H_{14}$  oligomer for the two sets of geometrical parameters. In general terms the same analysis applies to these results as for the  $C_{20}H_{22}$  oligomer. Tables V and VI give the correlated/CHF ratios for  $\alpha$  and  $\gamma$  of the  $C_{12}H_{14}$  and  $C_{20}H_{22}$  oligomers as a function of the method and geometry. The DFT methods show an increase in the ratio upon going from  $C_{12}H_{14}$  to  $C_{20}H_{22}$  while MP2 shows a small decrease or no change at all. Except for HFVWN and, perhaps, for the hybrid HF-DFT scheme, this increase with chain length is unreasonably large (in comparison with the MP2 result), particularly for  $\gamma$  and for the more alternant system.



TABLE V. Correlated/CHF ratio for the electronic static longitudinal polarizability of  $C_{12}H_{14}$  and  $C_{20}H_{22}$  using different correlation methods. See caption of Table I for basis set information.

		B3LYP/6-311G* geometry BLA = 0.065 Å	RHF/6-31G geometry BLA = 0.112 Å
MP2	$C_{12}H_{14}$	0.76	0.80
	$C_{20}H_{22}$	0.69	0.77
SVWN	$C_{12}H_{14}$	1.23	1.27
	$C_{20}H_{22}$	1.54	1.61
B3LYP (20%)	$C_{12}H_{14}$	1.15	1.17
	$C_{20}H_{22}$	1.35	1.36
HFVWN	$C_{12}H_{14}$	1.00	0.99
	$C_{20}H_{22}$	0.99	0.99
Hybrid HF-DFT (B3LYP)	$C_{12}H_{14}$	1.00	1.01
	$C_{20}H_{22}$	1.06	1.07
LDA/LDA	$C_{12}H_{14}$	1.33	1.32
	$C_{20}H_{22}$	1.56	1.62

#### IV. FURTHER DISCUSSION, CONCLUSIONS AND OUTLOOK

From these investigations, it turns out that all conventional and most nonconventional DFT functionals fail for linear and nonlinear responses of large  $\pi$ -conjugated systems. They fail in one or more of several ways: (i) the correlation correction to  $\alpha$  is either much too small or in the wrong direction, leading to an overestimate; (ii)  $\gamma$  is significantly overestimated; (iii) the chain length dependence is excessively large, particularly for  $\gamma$  and for the more alternant system; and (iv) the BLA effects on  $\gamma$  are either underestimated or qualitatively incorrect. The poor results with the LB94 potential show that the overestimations are not related to the asymptotic behavior of the potential, as it is the case for small molecules. There is one partial exception to these

TABLE VI. Correlated/CHF ratio for the electronic static longitudinal second hyperpolarizability of  $C_{12}H_{14}$  and  $C_{20}H_{22}$  using different correlation methods. See caption of Table I for basis set information.

		B3LYP/6-311G* geometry BLA = 0.065 Å	RHF/6-31G geometry BLA = 0.112 Å
MP2	$C_{12}H_{14}$	1.93	1.89
	$C_{20}H_{22}$	1.68	1.78
SVWN	$C_{12}H_{14}$	1.80	2.77
	$C_{20}H_{22}$	2.92	7.09
B3LYP(20%)	$C_{12}H_{14}$	1.81	2.38
	$C_{20}H_{22}$	2.82	4.65
HFVWN	$C_{12}H_{14}$	0.97	0.96
	$C_{20}H_{22}$	0.97	0.96
Hybrid HF-DFT (B3LYP)	$C_{12}H_{14}$	1.76	1.84
	$C_{20}H_{22}$	1.97	2.22
LDA/LDA	$C_{12}H_{14}$	1.87	3.05
	$C_{20}H_{22}$	3.13	7.44

TABLE VII. HOMO-LUMO gap of  $C_{20}H_{22}$  obtained by the CHF/6-31G and various DFT methods. See caption of Table I for basis set information. All the values are in eV.

	B3LYP/6-311G* geometry BLA = 0.065 Å	RHF/6-31G geometry BLA = 0.112 Å
RHF	6.85	7.65
S	1.28	1.61
B	1.30	1.64
HFVWN	6.90	7.71
HFLYP	6.85	7.65
SVWN	1.29	1.62
SLYP	1.28	1.61
SPW91	1.29	1.62
BVWN	1.30	1.65
BLYP	1.30	1.64
BPW91	1.31	1.65
B3LYP (20%)	2.21	2.68
B3LYP' (50%)	3.81	4.44
B3LYP'' (80%)	5.60	6.35
LDA	1.30	1.64
LB94	1.27	1.62

failures namely, in the case of  $\gamma$ , the hybrid HF-DFT methods give reasonable values. As a consequence of (ii) and (iii), for large oligomers the  $\gamma$  per unit cell is expected to be wrong by an order of magnitude or more when determined by conventional DFT procedures. This contrasts with the accuracy of many DFT schemes for structural properties of  $\pi$ -conjugated systems as well as for linear and nonlinear responses of small molecules.

Our original intent was to use DFT calculations as an aid in designing new NLO materials. The results presented here cause us to be skeptical about using currently available LDA and GGA functionals for this application. Although we have considered only electronic hyperpolarizabilities there are clear implications for vibrational hyperpolarizabilities as well since the latter depend on normal coordinate derivatives of the lower-order polarizabilities.<sup>44</sup>

It is not possible to blame the erroneous behavior of the GGA (and LDA) calculations to either incorrect modeling of only exchange, or of only correlation. The functionals that are denoted exchange and correlation do not describe these effects in the traditional sense. Correlation functionals with or without gradient corrections have very little effect upon both  $\alpha$  and  $\gamma$  and therefore do not model the electron correlation effects embodied for instance in MP2 calculations. On the other hand, the DFT exchange functionals do not appear to model these effects correctly either, since they are responsible for an increase instead of a decrease in  $\alpha$ , for a far too large increase in  $\gamma$ , and for the strange BLA effects on  $\gamma$ . This has been further supported by showing that the higher the percentage of HF-exchange, the smaller this incorrect behavior.

For improving the methodology, it is necessary to determine the problem with the currently available functionals and, particularly their functional derivatives which give the

exchange-correlation potential. Moreover, since the performance of the functionals seems to deteriorate with the extent of the conjugated PA chains, the question should be addressed as to why the deficiency is related to the chain length.

The problem of the LDA and GGA methods for computing  $\alpha$  may be related to the difficulty of determining the excitation energies in large polyenes. From the value of the HOMO-LUMO gap,  $\Delta E$ , listed in Table VII, one sees that for a given geometry the variations in  $\alpha$  and  $\gamma$  from one method to another parallel the variations in  $\Delta E$ , i.e., the smaller the  $\Delta E$  the larger the  $\alpha$  and  $\gamma$  values. In addition, within a given method  $\alpha$  and  $\Delta E$  vary consistently with BLA, i.e.,  $\alpha$  decreases when  $\Delta E$  increases, whereas for  $\gamma$ , surprisingly, an inverse relation has been found for the set of functionals SVWN, SLYP, SPW91, BVWN, BLYP, BPW91 and LDA/LDA, LB94/LDA, LB94/LB94. A simple partial fix, especially for linear polarizabilities, could be achieved by means of the scissors correction (i.e., a uniform shift of the virtual orbitals with respect to the occupied orbitals), which has been widely employed for calculating the dielectric constant of solids.<sup>71,72</sup> However, it is difficult to know *a priori* what shift to use for a given chain and how that shift should depend upon the chain length (see below for further discussion).

The inherent problem of conventional DFT approaches for determining (hyper)polarizabilities seems to be the short-sightedness of the XC-potentials, which mainly feel the local density and are relatively insensitive to the polarization charge induced by an external electric field at the extremities of the chain. This leads to excess charge at the chain ends and inadequate screening of that charge as one proceeds toward the center of the chain. As an illustration, we have carried out a Mulliken population analysis for  $C_{40}H_{42}$  in an external electric field of  $20 \times 10^4$  a.u. (a large amplitude was chosen to emphasize the effect). This field was applied along the longitudinal axis for both the RHF and SVWN treatments (see Fig. 2). In the RHF case, the screening is such that in the middle portion of the chain the electronic distribution is essentially periodic and the total charge of the unit cell is very small. On the other hand, there is a substantial charge polarization within each unit cell that is essentially the same throughout the central region of the chain. The unit cell polarization is defined as the difference of the Mulliken charges of the two CH groups of the unit cell. These results are in complete agreement with earlier work of André<sup>73</sup> and Kirtman.<sup>74</sup> The charge distribution obtained with the DFT-SVWN method is very different. Application of an external electric field breaks the periodicity of the electron distribution in the middle of the chain; and the unit cell charge evolves almost linearly with position along the chain demonstrating that the external electric field is screened only to a small extent. In addition, there is little charge polarization within the unit cell.

DFT schemes based on conventional XC functionals cannot correct the linear potential due to the applied field<sup>73-75</sup> as required neither for finite nor for infinite systems. In the solid state literature there has been recently much discussion about describing and solving this difficulty.

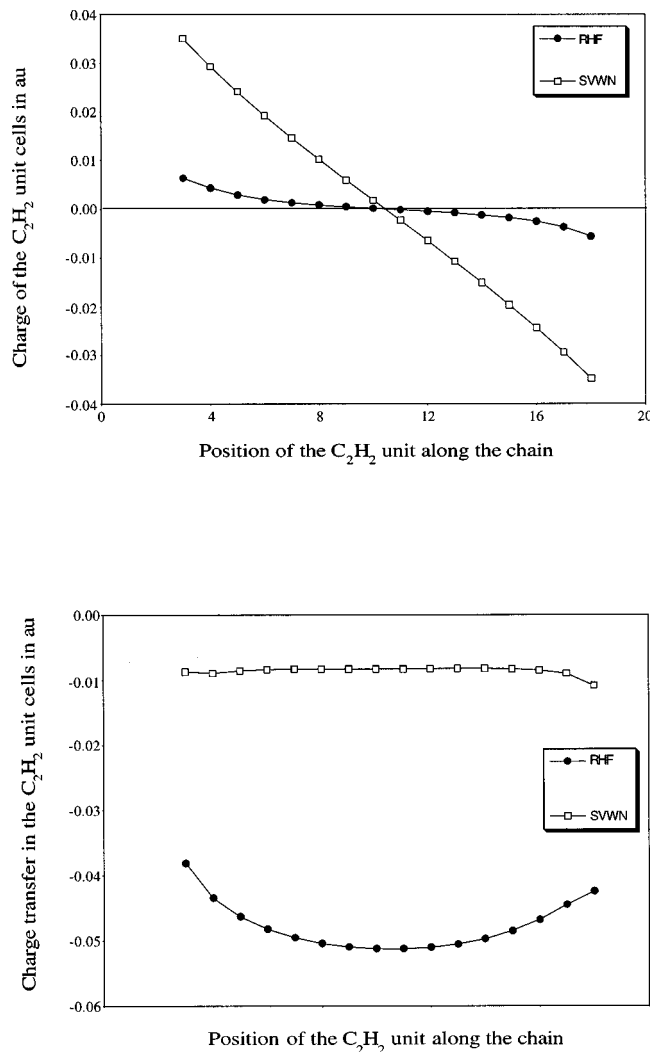


FIG. 2. (top) Total charge per  $C_2H_2$  unit cell and (bottom) polarization charge in the  $C_2H_2$  unit cell as a function of its position along the  $C_{40}H_{42}$  backbone computed at the RHF and SVWN levels of approximation using the 6-31G basis set within Mulliken population analysis. The charge polarization of a unit cell is defined as the charge difference between its constituting CH groups.

One way consists of adding a polarization-dependent (i.e., linear field) term to the exchange correlation functional<sup>76,77</sup> within the so-called polarization-dependent density-functional theory (PDDFT). As shown in Ref. 77 there is a close connection between PDDFT and the scissors approach, with the latter being based on quasiparticle theory. The problem with the former is that the polarization-dependent XC kernel is unknown; the difficulty with the scissors treatment is that it goes beyond Kohn-Sham theory and, furthermore, the choice of the shift remains uncertain.<sup>77,78</sup> Indeed, there is a significant difference between inorganic semiconductor and  $\pi$ -conjugated systems. In the case of Si, for example, the incorrect behavior of the exchange correlation potential leads to errors in the dielectric constant (polarizability) on the order of 10% whereas, for PA, it leads to errors larger than 100%. In a forthcoming paper, it will be investigated how such a linear term can arise in finite systems, and if the fact that LDA and GGA XC potentials miss such a term can be sufficient explanation for their incorrect density responses.

It will also be tested whether or not the Krieger–Li–Iafrate (KLI) potential<sup>79,80</sup> might cure the incorrect density response obtained in LDA or GGA schemes. This local X-only potential, which is an approximation to the exact local exchange potential, the OPM potential,<sup>81</sup> improves on the LDA and GGA potentials in several ways. Among other things, it includes self-interaction corrections (SIC)<sup>82</sup> and possesses the required integer particle discontinuity. It furthermore provides exchange energies which are very close to the HF exchange energies. Since it improves the band gap, at least in noble gas and in alkali halide solids,<sup>80</sup> it is therefore worthwhile to investigate if the KLI potential corrects the LDA and GGA results for  $\alpha$  and  $\gamma$ .

A better understanding of the incorrect density response to an external electric field in DFT calculations is clearly needed. Further detailed investigations are currently underway in our laboratories and our results will be the subject of a forthcoming paper.

## ACKNOWLEDGMENTS

The authors would like to acknowledge stimulating discussions with Professor J. M. André, Professor S. B. Trickey, Dr. D. H. Mosley, and Dr. R. van Leeuwen. B.C. and E.A.P. thank the Belgian National Fund for Scientific Research for their Research Associate and Scientific Collaborator positions, respectively. Calculations were performed on the IBM SP2 of the Namur Scientific Computing Facility (Namur-SCF), at the Maui High Performance Computing Center, on the IBM SP2 of the Stichting Academisch Rekencentrum Amsterdam (SARA), as well as using the W. M. Keck Computational Physics Laboratory (UNLV). B.C. and E.A.P. gratefully acknowledge the financial support of the FNRS-FRFC, the “Loterie Nationale” for the convention No. 2.4519.97 and the Belgian National Interuniversity Research Program on “Sciences of Interfacial and Mesoscopic Structures” (PAI/IUAP N° P4/10). S.v.G. gratefully acknowledges financial support from the Netherlands Organization for Scientific Research (NWO) through its foundations SON and NCF. C.S.G. thanks the NSF-EPSCoR for financial support.

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